succinimide[41]) was heated at 160–165° (10 mm), collecting the distillate in, first, a trap at 0°, then a second trap cooled in liquid nitrogen. There were 20 g of 1-bromo-2-methylene-3-butene obtained by this technique,[42] of bp 25° (10 mm), sufficiently pure for the next step. After purification by glpc on a silicone column, the compound had nmr, 4.05 (2 H, s, CH_2Br), 5.0–5.6 (4 H, m, $C{=}CH_2$), 6.33 (1 H, d of d, J = 10.5 and 17 Hz, $-CH{=}C$); mass spectrum 146/148 (28), 67 (100), 41 (51).

Anal. Calcd for C_5H_7Br: Br, 54.37. Found: Br, 53.19.

This compound was heated at reflux for 18 hr in 10 ml of ethanol with 1.64 g of anhydrous sodium acetate, then distilled. Redistillation gave 0.8 g of pure 1-acetoxy-2-methylene-3-butene, bp 72° (45 mm), of identical ir, nmr, and mass spectra with that obtained from dimethyl itaconate.[40] When the acetate was reduced with lithium alumin hydride in ether, a product (**35**) of identical properties with that described by Bailey, *et al.*,[40] was obtained.

When this compound was treated under the usual conditions with 1-ethoxy-2-methyl-1,3-butadiene, only traces (glpc) of the aldehyde **36** were obtained.

Acknowledgment. The author is greatly indebted to Professor A. Eschenmoser for helpful discussions during this work, and to Dr. M. Stoll and the directors of Firmenich & Cie, for encouragement and support.

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[41] R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082, 1441 (1956).

[42] G. B. Butler and R. M. Ottenbrite, *Tetrahedron Letters*, 4873 (1967), report a similar preparation of 1,4-dibromo-2,3-dimethylenebutane.

A Novel Synthesis of Substituted Allenes[1]

Peter Rona[2] and Pierre Crabbé

Contribution from the Research Laboratories, Syntex, S.A., Mexico, D. F., Mexico.

Received December 21, 1968

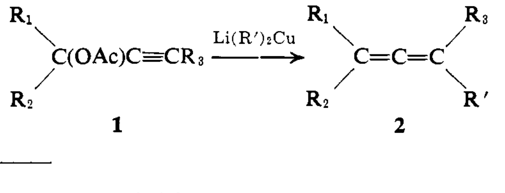
Abstract: Alkyl allenes were obtained by the reaction of 1-ethynylcycloalkanol acetates with the organocopper reagents, $LiMe_2Cu$ and Li-n-Bu_2Cu. Reactions of steroidal ethynylcarbinol acetates show that the reaction is not stereoselective. The functional group specificity of the organocopper reagents and the scope of the reaction are outlined.

Although allenes were characterized long ago as a distinct class of organic compounds, they have received only limited attention from organic chemists.[3] Even at the present time, the more common synthetic methods for the preparation of alkylallenes present a number of inherent difficulties when applied to complicated polyfunctional molecules.

In connection with some studies with the organocopper(I) reagent[4,5] we observed the ready transformation of ethynylcarbinol acetates to alkyl allenes.

In this paper we wish to report full details of our novel allene synthesis,[6] as well as additional findings obtained recently.

The general applicability of the organocopper(I) reagents for the synthesis of alkylallenes **2**, from substituted ethynylcarbinol acetates **1** was tested by the transformations listed in Table I.



$$R_1R_2C(OAc)C{\equiv}CR_3 \xrightarrow{Li(R')_2Cu} R_1R_2C{=}C{=}CR_3R'$$

1 **2**

These results (Table I) show that secondary, tertiary, and quaternary nonterminal allenes are obtained in fair to high yields by this method. No allenic product could be isolated from the reaction of 1-ethynylcyclohexanol acetate (**5**), with methyllithium alone, thus the reaction is not effected by the latter reagent. As expected, allenic material was not isolated from the reaction of 1-hexyne with $LiMe_2Cu$, indicating that an appropriate leaving group is necessary for the formation of the allene system. That the structure of the leaving group is of considerable importance is indicated by the absence of allenic material in the product of reaction 1-ethynylcyclohexanol (**9**) and lithium dimethylcopper(I).

The organocopper(I) compounds reported in organic synthesis (excluding reactions of organomagnesium halides with catalytic amounts of copper compounds present), to our knowledge, are the methyl, ethyl, and butyl derivatives.[4,7–9]

Our findings suggest that the lithium di-n-butylcopper(I) (Li-n-Bu_2Cu) compound behaves in a manner analogous to the $LiMe_2Cu$ reagent. Thus the compound obtained from the reaction of equimolar amounts of n-butyllithium and copper(I) iodide did not react with 1-ethynylcyclohexanol acetate (**5**), whereas the product of the reaction of 2 mol equiv of n-butyllithium with 1 mol equiv of copper(I) iodide reacted with the substituted ethynylcarbinol acetates **5** and **11** to produce allenes (Table I).

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[1] Publication No. 354 from the Syntex Institute of Steroid Chemistry. For No. 353, see: P. Rona, L. Tökes, J. Tremble, and P. Crabbé, *Chem. Commun.*, 43 (1969).

[2] Syntex Postdoctoral Research Fellow, 1967–1968.

[3] (a) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967), and references cited therein; (b) K. Griesbaum, *Angew. Chem. Int. Ed. Engl.*, **5**, 933 (1966); (c) M. V. Mavrov and V. F. Kucherov, *Russ. Chem. Rev.*, **36**, 233 (1967); (d) M. Bertrand, *Bull. Soc. Chim. Fr.*, 3044 (1968); (e) See also: H. Fischer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 13.

[4] This study was stimulated by the reported exchange of halogen by alkyl with this reagent, see: E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

[5] P. Rona, L. Tökes, J. Tremble, and P. Crabbé, *Chem. Commun.*, 43 (1969).

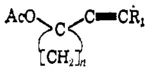
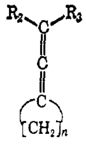
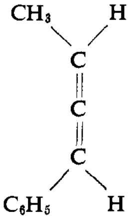
[6] For a preliminary communication, see: P. Rona and P. Crabbé, *J. Amer. Chem. Soc.*, **90**, 4733 (1968).

[7] H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966), and references therein.

[8] J. A. Marshall and H. Roebke, *ibid.*, **33**, 840 (1968).

[9] H. O. House and W. F. Fisher, Jr., *ibid.*, **33**, 949 (1968).

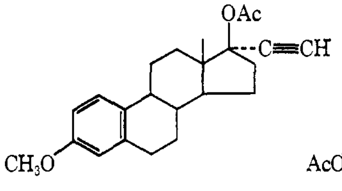
Table I. Conversion of Ethynylcarbinol Acetates into Allenes

Starting material 	Reagent	Product 	Yield, %
3, $n = 4$; $R_1 = H$	$LiMe_2Cu$	**4**, $n = 4$; $R_2 = H$; $R_3 = Me$	81
5, $n = 5$; $R_1 = H$	$LiMe_2Cu$	**6**, $n = 5$; $R_2 = H$; $R_3 = Me$	85
7, $n = 6$; $R_1 = H$	$LiMe_2Cu$	**8**, $n = 6$; $R_2 = H$; $R_3 = Me$	82
5, $n = 5$; $R_1 = H$	Li-*n*-Bu_2Cu	**10**, $n = 5$; $R_2 = H$; $R_3 =$ *n*-Bu	65
11, $n = 5$; $R_1 = Me$	$LiMe_2Cu$	**12**, $n = 5$; $R_1 = R_2 = Me$	71
11, $n = 5$; $R_1 = Me$	Li-*n*-Bu_2Cu	**13**, $n = 5$; $R_1 = Me$; $R_2 =$ *n*-Bu	80
14, $n = 5$; $R_1 =$ *n*-Bu	$LiMe_2Cu$	**13**, $n = 5$; $R_1 = Me$; $R_2 =$ *n*-Bu	47
$C_6H_5CH(OAc)C\equiv CH$ **15**	$LiMe_2Cu$	 **16**	38[a]

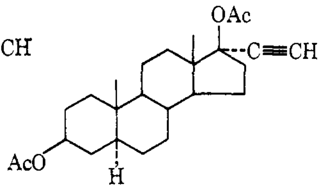
[a] F. Acree, Jr., and F. B. LaForge, *J. Org. Chem.*, **4**, 569 (1939). The low yield of this compound is probably due to its known tendency to polymerize.

Stereochemistry and Mechanism

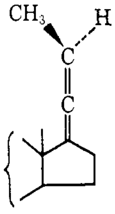
Reaction of the acetates **17** and **18**, yielded 2:3 mixtures of the corresponding methylallenes **19** and **20**, and **21** and **22**.



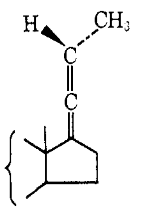
17, estrone series



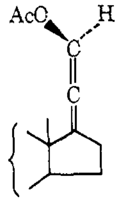
18, androstane series



19, estrone series
21, androstane series



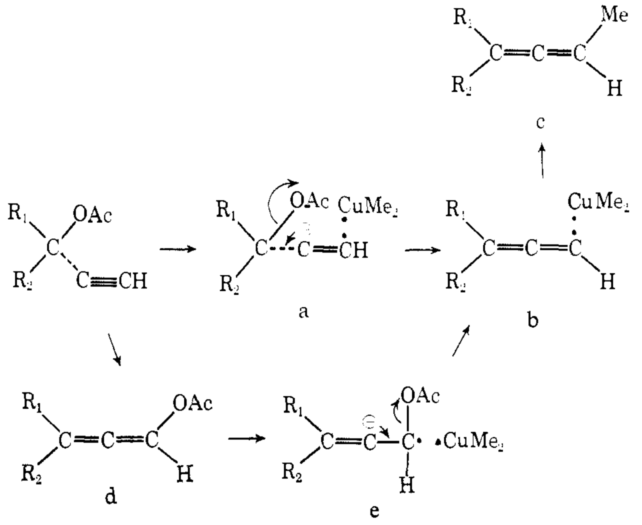
20, estrone series
22, androstane series



23, estrone series
24, androstane series

Formation of the allene system appears to be facilitated by a synergistic effect brought about by the reagent, acting on the triple bond and the acetoxyl group.[10] Furthermore, we found that the stereochemically pure allenic acetates **23** and **24**,[11,12] on reaction with the $LiMe_2Cu$ reagent, yielded a mixture of the corresponding isomeric methylallenes **19** and **20**, and **21** and **22**.

The reaction of lithium dialkylcopper with ethynylcarbinol acetates probably proceeds by electron transfer of the reagent to the acetylene, followed by explusion of the acetate and transfer of a methyl radical (*cf.* a → b → c). Intermediate b can also arise from the isomeric allenyl acetate d by electron transfer to the center carbon of the allene system e. The geometry of the intermediate radical b is apparently not maintained, since a mixture of stereoisomeric alkyl allenes is formed.



The mechanism herein proposed is consistant with the suggested mechanism of 1,4 addition of alkyl groups to enones brought about by alkylcopper reagents.

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(10) *Inter alia:* (a) R. E. Dessy and F. E. Paulik, *J. Amer. Chem. Soc.*, **85**, 1812 (1963); (b) R. E. Dessy, T. Hieber, and F. E. Paulik, *ibid.*, **86**, 28 (1964); (c) J. J. Eisch and G. R. Husk, *ibid.*, **87**, 4194 (1965), and references cited therein.

(11) V. T. Ramakrishnan, K. V. Narayanan, and S. Swaminathan, *Chem. Ind.* (London), 2082 (1967).

(12) (a) W. R. Benn, *J. Org. Chem.*, **33**, 3113 (1968); (b) M. Biollaz, H. Carpio, P. Crabbé, A. Failli, P. Rona, E. Velarde, and J. H. Fried, in preparation.

Lithium dimethylcopper may be used with acetylenic compounds containing a (nonallylic) acetoxy group for introduction of the allene moiety. It may also be used for conjugate methylation of α,β-unsaturated ketones. Unprotected alcohol groups are unreactive, as shown by the attempted reactions of 1-ethynylcyclohexanol with the $LiMe_2Cu$ reagent. Previous studies have shown that saturated ketones are not atttacked by the reagent.[7,8]

Experimental Section[13]

1-(1-Propynyl)cyclohexanol Acetate (11). A solution of 1-(1-propynyl)cyclohexanol,[14] (10 g) in dry pyridine (100 ml) and acetic anhydride (50 ml), was heated to reflux for 4 hr under nitrogen. The solvents were distilled off under vacuum (10 mm). The residue was distilled giving pure **11** (8.4 g) as a colorless oil, bp 67° (0.5 mm); $n^{25}\text{D}$ 1.4727; ir 2210 (C≡C) and 1725 cm^{-1} (C=O); nmr ($CDCl_3$) 1.3–1.7 broad m ($-CH_2-$), 1.85 s ($C{\equiv}CCH_3$), and 1.95 s ($COCH_3$). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; mol wt, 180.2. Found: C, 72.79; H, 8.95; mol wt, 180 (ms).

1-(1-Hexynyl)cyclohexanol. To a solution of ethylmagnesium bromide (3 *N*; 81 ml) in ether, in a three-necked flask equipped with a mechanical stirrer, Dry Ice condenser and cooled in an ice–salt bath, a solution of 1-hexyne (20 g) in ether (100 ml) was slowly added from a dropping funnel, the reaction mixture being kept under nitrogen. After the initial strong reaction had taken place, the mixture was heated to reflux for 2 hr and after cooling in an ice bath, a solution of cyclohexanone (26.2 g) in ether (150 ml) was slowly added. After leaving the reaction mixture at room temperature overnight, it was cooled in an ice bath and decomposed by addition of saturated ammonium chloride solution, and the product was extracted with ether. The ether extract was washed with water and dried ($MgSO_4$). The residue left after evaporation of the ether on distillation gave pure 1-(1-hexynyl)cyclohexanol (26 g), bp 83° (0.5 mm), $n^{24}\text{D}$ 1.4801. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18; mol wt, 180.2. Found: C, 79.86; H, 11.10; mol wt, 180 (ms).

1-(1-Hexynyl)cyclohexanol Acetate (14). 1-(1-Hexynyl)cyclohexanol (10 g) was esterified as in **11** to afford pure **14** (8.4 g) as a colorless oil, bp 73° (0.5 mm); $n^{24}\text{D}$ 1.4670; ir 2230 (C≡C) and 1742 cm^{-1} (C=O); nmr ($CDCl_3$) 0.9 m (CH_2CH_3), 1.2–1.7 broad unresolved band ($-CH_2-$), and 1.98 s ($COCH_3$). *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97; mol wt, 222.3. Found: C, 75.41; H, 9.88; mol wt, 222 (ms).

Cyclopentylidenebuta-1,2-diene (4). Ether (200 ml) was distilled from lithium aluminium hydride, into a three-necked flask, equipped with a magnetic stirrer, dropping funnel, condenser, and a nitrogen trap. Cuprous iodide (10.4 g) and methyllithium solution in ether, were introduced into the flask and the dropping funnel, respectively, against a current of nitrogen. The flask was cooled in an ice–salt bath and the methyllithium solution was added dropwise, to the vigorously stirred suspension of cuprous iodide. The heavy yellow precipitate that appeared, dissolved on continued addition of the methyllithium solution, leaving a colorless solution, at which point the addition was stopped. To the stirred and cooled (ice–salt bath) solution of the reagent, 1-ethynylcyclopentanol acetate (**3**)[15] (7.6 g) in ether (120 ml, freshly distilled from lithium aluminium hydride) was added from an equilibrated dropping funnel. The stirred reaction mixture was kept in an ice bath for 5 hr, a saturated solution of ammonium chloride was added, the organic layer was separated and the dark blue aqueous layer was extracted three times with ether. The ether extracts were dried ($MgSO_4$) and filtered, and the ether was distilled off. On distillation of the residue, **4** (6.0 g) was obtained, bp 45–50° (13 mm); $n^{25}\text{D}$ 1.4903; ir 1958 cm^{-1} (C=C=C); nmr ($CDCl_3$) 1.60 d (*J* = 7 Hz, $-CH_3$), 1.6–1.8 broad m ($-CH_2{+}CH_2C{=}$), 2.15–2.55 broad m ($-CH_2C{=}$), and 4.75–5.25 m (=C*H*–). *Anal.* Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.41; H, 11.17.

Cyclohexylidenebuta-1,2-diene (6). 1-Ethynylcyclohexanol acetate (**5**)[16] (8.3 g) was treated as described for **4** to provide **6** (5.1 g) as a colorless oil, bp 55° (13 mm); $n^{20}\text{D}$ 1.4941; ir 1958 cm^{-1} (C=C=C); nmr ($CDCl_3$) 1.45–1.65 broad m ($-CH_2CH_2CH_2C{=}$), 1.62 d (*J* = 7 Hz, $-CH_3$), 1.9–2.2 broad m ($CH_2C{=}$), and 4.8–5.1 m (=CH–). *Anal.* Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.34; H, 11.29.

Cycloheptylidenebuta-1,2-diene (8). Treatment of 1-ethynylcycloheptanol acetate (**7**)[17] (9.1 g) as above gave **8** (4.2 g), bp 90–92° (15 mm); $n^{22}\text{D}$ 1.4944; ir 1958 cm^{-1} (C=C=C); nmr ($CDCl_3$) 1.50–1.65 broad m ($-CH_2-$), 1.60 d (*J* = 7 Hz, $-CH_3$), 2.1–2.4 broad m ($-CH_2C{=}$), and 4.7–5.1 m (=CH–). *Anal.* Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.73; H, 12.19.

3-Methylcyclohexylidenebuta-1,2-diene (12). Similarly, **11** (1.81 g) provided **12** (0.96 g), bp 65° (12 mm); $n^{25}\text{D}$ 1.4870; ir 1960 cm^{-1} (C=C=C); nmr ($CDCl_3$) 1.3–1.7 broad m ($-CH_2-$), 1.65 s ($-CH_3$), 2.03 broad m ($-CH_2C{=}$). *Anal.* Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84; mol wt, 136.2. Found: C, 88.38; H, 11.71; mol wt, 136 (ms).

Phenylbuta-1,2-diene (16). Phenylethynylcarbinol acetate (**15**)[18] (2.8 g) furnished the crude product **16**[19] (0.79 g), bp 84° (4 mm); $n^{26}\text{D}$ 1.5664; ir 1950 cm^{-1} (C=C=C). The compound polymerizes on being left for a short time at room temperature. The highest peak in the ms at *m/e* 260 corresponds to the dimer. Nmr of a mixture of the monomer and the dimer ($CDCl_3$) showed: 1.3–1.7 unresolved broad m, 1.7 q (center), bands near 5.0, 6.0, and 6.9, and aromatic protons at 7.2 ppm.

Cyclohexylidenehepta-1,2-diene (10). Li-*n*-Bu_2Cu reagent was prepared from cuprous iodide (10.4 g) in ether (300 ml) and *n*-butyllithium in hexane (35 ml, 22.2 wt %). The reagent was prepared using the same technique employed in the preparation of the $LiMe_2Cu$ reagent. To the cooled (ice–salt bath), black solution of the reagent 1-ethynylcyclohexanol acetate[18] (4.15 g) in ether (100 ml) was added. The reaction mixture was cooled 0.5 hr in an ice–salt bath and left at room temperature, with stirring, for 4.5 hr. After usual work-up and distillation **10** (2.69 g) was obtained: bp 70° (1.5 mm); $n^{27}\text{D}$ 1.4770; ir 1950 cm^{-1} (C=C=C); nmr ($CDCl_3$) 0.8–1.0 broad m ($-CH_3$), 1.2–1.7 broad m ($-CH_2-$), 1.85–2.3 broad m ($-CH_2C{=}$), and 4.8–5.3 m (=CH). *Anal.* Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27; mol wt, 164.3. Found: C, 87.13; H, 12.36; mol wt, 164 (ms).

3-Methylcyclohexylidenehepta-1,2-diene (13). a. 14 (2.22 g) treated with $LiMe_2Cu$ as above provided **13** (1.6 g): bp 66° (0.7 mm); $n^{27}\text{D}$ 1.4800; ir 1955 cm^{-1} weak band (C=C=C); nmr ($CDCl_3$) 0.7–1.0 broad m ($-CH_2CH_3$), 1.1–1.7 broad m ($-CH_2-$), 1.62 s ($=CCH_3-$), and 1.95–2.20 broad m ($=CCH_2-$). *Anal.* Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44; mol wt, 178.3. Found: C, 87.60; H, 12.37; mol wt, 178 (ms).

b. Reaction of **11** (1.82 g) with Li-*n*-Bu_2Cu gave compound **13** (0.7 g): bp 58–63° (0.5 mm); $n^{29}\text{D}$ 1.4801. The ir spectrum is superimposable on that of the product from procedure a. The material is homogenous on vpc on a dinonylphthalate column the retention time being equal to that of the product from procedure a.

Reaction of 1-Hexyne with $LiMe_2Cu$. Treatment of 1-hexyne (2.7 g) as in **4** gave a crude product which was distilled and collected in three fractions: bp 78–82° (580 mm), bp 76–80° (200 mm), and bp 100–105° (2 mm). The ir spectra (neat liquid) of none of the fractions contained an allene band.

Reaction of 1-Ethynylcyclohexanol Acetate (5) with Methyllithium. To a stirred solution of the reagent (28 ml of a 1.7 *M* solution of methyllithium in ether was added to 200 ml of dry ether) a solution of 1-ethynylcyclohexanol acetate (**5**) (3.32 g) in ether (100 ml) was added. After cooling in an ice–salt bath for 0.5 hr, the

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[13] Melting points are uncorrected and were taken on a Fisher-Johns apparatus. Optical rotations were measured at 27° in chloroform solution on an O. C. Rudolph and Sons polarimeter. Ultraviolet (uv) spectra were measured in ethanol on a Beckman DU Model 2400 spectrometer. Infrared (ir) spectra were measured as KBr disks (for solids), or neat, unless otherwise stated, for liquids on a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were recorded on Varian HA-100 and A-60 spectrometers using deuteriochloroform as solvent. Chemical shifts are reported in parts per million (ppm) relative to TMS on the δ scale to the nearest 0.01 ppm. Coupling constants are reported in hertz (Hz); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra (ms) were measured on an Atlas CH-4 spectrometer equipped with TO-4 ion source. The ionizing energy was maintained at 70 eV and the ionizing current at 10 μA. We wish to thank Miss J. Tremble, Dr. L. Tökes, and Dr. L. Throop, Analytical Department, Syntex Research, Palo Alto, Calif., for assistance with some of these measurements.

[14] M. D. Cameron, U. S. Patent 3,153,097 (Oct 13, 1964); *Chem. Abstr.*, **62**, 1579*h* (1965).

[15] A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 2247 (1953).

[16] H. Rupe, W. Messner, and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

[17] G. Voigt and H. Pfanz, East German Patent 14182 (Dec 1957); *Chem. Abstr.*, **53**, 13080*f* (1959).

[18] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733 (1942).

[19] See Table I, footnote *a*.

reaction mixture was left at room temperature for 4 hr. On usual work-up, only 1-ethynylcyclohexanol (**9**) (1.5 g) was isolated.

3-Methoxy-17-(2′β-methylethenylidene)estra-1,3,5(10)-triene (19) and 3-Methoxy-17-(2′α-methylethenylidene)estra-1,3,5(10)-triene (20). a. To a solution of the LiMe$_2$Cu reagent prepared as indicated above, 3-methoxy-17-(α-ethynyl)estra-1,3,5(10)-triene-17β-ol acetate (**17**) (2.0 g) was added. Chromatography gave the crystalline product **19** (0.254 g) and the starting material **17** (0.454 g). On six recrystallizations from methanol a small amount of **19** was obtained, mp 125–127°; $[\alpha]_D$ +81° (CHCl$_3$); ir 1957 cm^{-1} (C=C=C); $\lambda_{\max}^{\mathrm{EtOH}}$ 278 (ϵ 2090) and 287 mμ (ϵ 1860); nmr (100 MHz) 0.895 s (18 H), 1.640 d (J = 7 Hz, 21 H), 3.770 s (-OCH$_3$), 5.05–5.30 m (20 H), and 6.6–7.3 aromatic protons. *Anal.* Calcd for C$_{22}$H$_{28}$O: C, 85.66; H, 9.15; mol wt, 308.4. Found: C, 85.61; H, 9.22; mol wt, 308 (ms).

The material that remained in the mother liquor has identical R_f value and uv spectrum to **19**, ir 1951 cm^{-1} (C=C=C). It is a mixture of **19** and **20**, of which compound **20** could not be isolated neither by recrystallization, nor by column, or preparative thin layer chromatography (tlc). From the nmr spectrum (100 MHz) of this mixture, the chemical shifts corresponding to **20** are: 0.86 s (18 H), 1.66 d (J = 7 Hz, 21 H), 3.77 s (OCH$_3$), 4.78–5.14 m (20 H), and 6.6–7.3 aromatic absorption (CDCl$_3$).

b. In a similar fashion 3-methoxy-17-(2′β-acetoxyethenylidene)-estra-1,3,5(10)-triene (**23**) (1.6 g) afforded a crystalline product (0.35 g). The material is a mixture of **19** and **20**. Neither of the components could be isolated in a pure form, either by column or tlc, or by recrystallization. On repeated recrystallization from methanol mixtures ranging from mp 57–59°, $[\alpha]_D$ +19°, to mp 116–118°, $[\alpha]_D$ +69°, were obtained. The uv spectra and R_f value are identical with those of the mixtures obtained by procedure a; ir 1957 cm^{-1} (C=C=C). The nmr spectrum (100 MHz, CDCl$_3$) is identical with that of the mixture of **19** and **20**, obtained from procedure a, with the major component being **20**, the ratio of **20** to **19** in the product is approximately 2:1.

3β-Acetoxy-17-(2′β-methylethenylidene)-5α-androstane (21) and 3β-Acetoxy-17-(2′α-methylethenylidene)-5α-androstane (22). a. Reaction of 3β,17β-diacetoxy-17α-ethynyl-5α-androstane (**18**) (2.3 g) provided a product (1.95 g) which was chromatographed on a column (from 100 g of florosil, in hexane). Elution with hexane–ether (95:5) gave the crystalline product (1.495 g). This material is homogenous on tlc, however it was a mixture of **21** and **22**, the pure components could not be separated by preparative tlc, column chromatography, or recrystallization. After ten recrystallizations from methanol, a material, mp 137.5–139°, was obtained—the melting point of this material could not be raised by further recrystallization; $[\alpha]_D$ +19° (CHCl$_3$); ir 1961 cm^{-1} (C=C=C); nmr (100 MHz) (the material is a mixture of **21** and **22**) 0.740 s (19 H), 0.847 s (18 H, **22**), 0.881 s (18 H, **21**), 1.688 d (J = 7 Hz, 22 H, **21**), 1.722 d (J = 7 Hz, 22 H, **22**), 2.030 s (-COCH$_3$), 4.60–5.05 m (3α H), and 5.10–5.45 m (21 H) (pyridine-d_5). Nmr (100 MHz) of the product, as obtained from column chromatography, indicates the presence of **22** and **21** in a ratio of approximately 3:2. *Anal.* Calcd for C$_{24}$H$_{36}$O$_2$: C, 80.85; H, 10.18; mol wt, 356. Found: C, 80.79; H, 9.76; mol wt, 356 (ms).

b. To the LiMe$_2$Cu reagent prepared as above, 3β-acetoxy-17-(2′β-acetoxyethenylidene)-5α-androstane (**24**) (0.58 g) was added. The reaction performed in the usual manner gave the crystalline product. The material has ir spectrum superimposable with the product obtained in procedure a. Similarly R_f values and nmr spectra (100 MHz, pyridine-d_5) of the products from both procedures are equal. The nmr spectrum indicates that **21** and **22** are present in approximately the same ratio as in the product obtained by procedure a.

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Unsaturated Neopentyl Compounds. The Effect of Methyl Substitution on the Acetolysis Rates of Homoallenic Neopentyl-Type Brosylates

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Abstract: A series of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonates with methyl substituents at C-3 and/or C-5 have been prepared and their solvolysis rates determined in buffered, anhydrous acetic acid. A Taft–Streitwieser treatment has been used to estimate that homoallenyl participation enhances the reaction rates by factors of 6200–170,000 times, and to deduce that the additional rate increases caused by 3-methyl substitution are due entirely to steric effects. It is suggested that the transition state of the rate-limiting step in each case is of the homoallyl–cyclopropylcarbinyl type with most of the charge concentrated at the vinyl position, C-4.

In a previous paper[1] we reported an example of homoallenyl participation in the solvolysis of a neopentyl-type brosylate, but were unable on the basis of our limited data to say much about the nature of the charge delocalization in the rate-limiting transition state. In order to be able to apply the technique of successive methyl substitution[2] to this problem we have prepared and determined the acetolysis rates of several methyl substituted homoallenic neopentyl-type brosylates.

Methods and Results

The required carboxylic acids and brosylates were prepared from the homoallenic aldehydes obtained *via* the Claisen–Cope rearrangement of propargyl vinyl ethers[3] derived from the *p*-toluenesulfonic acid catalyzed

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